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An optical study of single pentacene molecules in *n*-tetradecane

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Abstract

We report the spectroscopic observation of single pentacene molecules in the matrices *n*-tetradecane and *n*-hexadecane, using a confocal microscope operating at liquid-helium temperatures. A maximum detected photon emission rate of only 30 counts per second (cps) is found for pentacene in *n*-hexadecane and 160 cps for pentacene in *n*-tetradecane. For the latter system, the low count rate is shown to be caused by a high $S_1 \rightarrow T_1$ intersystem crossing yield of about 40% in combination with a triplet lifetime of 33 ± 3 μs. Pentacene molecules in this polycrystalline host are found to show little spectral diffusion on a timescale of seconds.

1. Introduction

As early as 1952, Shpol'skii reported low-temperature fluorescence spectra of polycyclic aromatic hydrocarbons dissolved in *n*-alkanes that showed remarkably narrow vibronic lines [1]. Following the observation of this so-called Shpol'skii effect, *n*-alkanes have been extensively used as a host for spectroscopic studies [2,3]. On the one hand, emphasis has been on the solute molecules because the increased resolution facilitates the analysis of the electronic spectra (e.g., of polycyclic aromatic hydrocarbons). On the other hand, the origin of the Shpol'skii effect has been addressed, and the linewidth was found to depend strongly on the guest/host combination, the rate of cooling, and the concentration. Rapid cooling produces a polycrystalline matrix and the spectral lines become narrow because of the weak interaction between the matrix and the chromophore embedded in a limited number of well-defined sites. Further understanding of the Shpol'skii effect would largely benefit from studies on a molecular scale.

A recent tool to study condensed matter on a molecular scale is single-molecule spectroscopy (for a review, see Ref. [4]). When the first spectra of single terrylene molecules in the Shpol'skii matrix *n*-hexadecane were reported [5], a study of the Shpol'skii effect on a microscopic scale was thought to be within reach. However, since then, only a few molecules (dibenzanthanthrene [6], diphenyloctatetraene [7], perylene [8], benzodiphenanthrobisanthene [9] and terrylenediimide [10]) have been found to match in these solvents the stringent conditions re-

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quired to collect the fluorescence signal from a single molecule. Oddly enough, pentacene, which was the pioneer molecule of single-molecule experiments in the condensed phase [11,12], has not yet been observed as a single molecule in a Shpol'skii system.

The present Letter concerns a preliminary report of a project that aims at studying the structure of Shpol'skii matrices using single-molecule spectroscopic and microscopic methods. For this purpose, pentacene seems to be a logical choice. It was the first molecule in condensed-phase single-molecule spectroscopy, and its photophysical properties are well known. Pentacene is a planar, linear, catacondensed aromatic molecule and, compared to the other molecules used for single-molecule spectroscopy, is expected to introduce a minimum perturbation of the structure and the dynamics of the polycrystalline *n*-alkane matrix. Here we present the optical detection of single pentacene molecules in the Shpol'skii matrices *n*-tetradecane and *n*-hexadecane. We have investigated these systems by excitation spectroscopy and have found low fluorescence count rates which will be discussed in relation to the intersystem-crossing (ISC) efficiency and the triplet lifetime. As a first step towards the study of the structure and the dynamics of the host matrix, we discuss the spectral diffusion observed for the pentacene probe.

2. Experimental

The single-molecule setup, described in detail elsewhere [13], can be summarized as follows. A single-mode dye laser (Coherent, 899-21) was stabilized in intensity by an electro-optical modulator (EOM, ConOptics) and its output was directed via a polarization preserving single-mode fiber to a confocal detection arrangement. The absolute frequency of the laser was obtained by recording the excitation spectrum of iodine. All the experiments were carried out at about 1.2 K with the sample mounted in a helium bath cryostat. Inside the cryostat, either an aspheric single lens (Thorlabs) or a microscope objective (Newport $\times 60$) focused the excitation beam to a spot of about 1 μm diameter. The sample position could be adjusted mechanically in a horizontal plane, both perpendicular to and along the optical axis, with an accuracy of about 1 μm. The same optics used to focus the beam collects the fluorescence which is selected by a dichroic mirror (DRLP590) and a long-pass filter (EFLP 610) and detected on an avalanche photodiode (EG & G SPCM-AQ-161). Photon counts were read by a multichannel scaling card (EG&G 923 MCS-plus) configured for continuous circularly buffered counting. The whole experiment was controlled and processed through a computerized data acquisition system [14].

We used a saturated solution ($\sim 10^{-6}$ mol mol^{-1}) of pentacene in either *n*-tetradecane or *n*-hexadecane which was deposited onto a circular LiF substrate. A thin quartz cover plate (100 μm) was used to protect the sample when plunged into liquid nitrogen and to ensure that the liquid forms a thin film with a typical thickness of some tens of micrometers. The sample holder was inserted quickly into the pre-cooled (77 K) cryostat. This fast cooling should lead to non-equilibrium polycrystalline mixed crystals.

3. Results and discussion

First we have investigated the fluorescence spectra of an ensemble of pentacene molecules in *n*-decane, *n*-undecane, *n*-dodecane, *n*-tetradecane and *n*-hexadecane. All these systems give rise to a Shpol'skii effect, and the linewidth of the 0–0 transition increases the longer the alkane suggesting that the Shpol'skii effect becomes weaker. According to the key-and-hole principle [15], *n*-undecane should offer the best environment (long axis pentacene 1.56 nm, *n*-undecane 1.55 nm), nevertheless the Debye–Waller factor is the smallest in this matrix. In each system, we have searched for single molecules, and in *n*-hexadecane and in *n*-tetradecane single molecules could be detected. In the longest *n*-alkane, the count rate was so low (30 cps) that we have limited the subsequent experiments to pentacene in *n*-tetradecane.

The excitation spectrum of pentacene in *n*-tetradecane (Fig. 1) shows a strong 0–0 line at 17 096 cm^{-1}. From comparison with the emission spectrum (not shown), we assign the line at a distance of 66 cm^{-1} to a phonon side band and the transition at a distance of 260 cm^{-1} to a vibronic line (accompa-

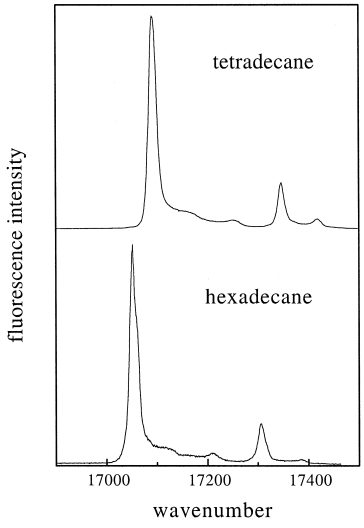

Fig. 1. Excitation spectra at 1.2 K of an ensemble of pentacene molecules embedded in the matrices *n*-tetradecane (top) and *n*-hexadecane (bottom) (concentration $\sim 10^{-6}$ mol mol^{-1}).

nied by its phonon side band). Two high-resolution fluorescence-excitation spectra of a single pentacene molecule are displayed in Fig. 2. At low excitation power, the spectrum shows a width of 10 MHz, close to the homogeneous linewidth of pentacene in *p*-terphenyl (about 8 MHz [16]). The second spectrum, recorded at higher excitation power, corresponds to saturation conditions and shows line broadening. Even for saturation, the detected photon count rate is as low as 140 cps. As it is not very likely that the radiative lifetime in this solvent differs significantly from the value obtained in *p*-terphenyl [17], the low

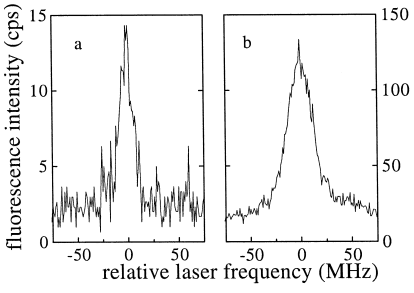

Fig. 2. Fluorescence-excitation spectra of a single pentacene molecule at 1.2 K. (a) Under non-saturating conditions (excitation intensity 3 mW cm^{-2}, 300 scans of 2 s); (b) under saturating conditions (excitation intensity 350 mW cm^{-2}, 500 scans of 1s). The centre position of the laser corresponds at 17093.6 cm^{-1}.

emitted photon rate is probably due to saturation starting at low excitation intensities. In Fig. 3a the linewidth Γ and the detected emission rate R are plotted as a function of excitation intensity. The solid curves represent non-linear least-squares fits to the data using the saturation expressions for the emission rate $R = (I/I_s)[R_\infty/(1 + I/I_s)]$, and for the linewidth $\Gamma = \Gamma_0\sqrt{1 + I/I_s}$, where I_s is the saturation intensity, R_∞ the maximum emission rate, and Γ_0 the homogeneous linewidth [16]. We find for this molecule a homogeneous linewidth of 8.1 MHz, a saturation intensity of 7 mW cm^{-2} and a saturated count rate of 148 cps. Maximum count rates between 70 and 160 cps have been found for all the molecules investigated and randomly distributed in the 0–0 absorption line.

We have measured the saturation curve for 12 different molecules – some being on the red and others on the blue side of the inhomogeneous band. The values found for the saturation intensity show a spread due to the distribution of the relative orienta-

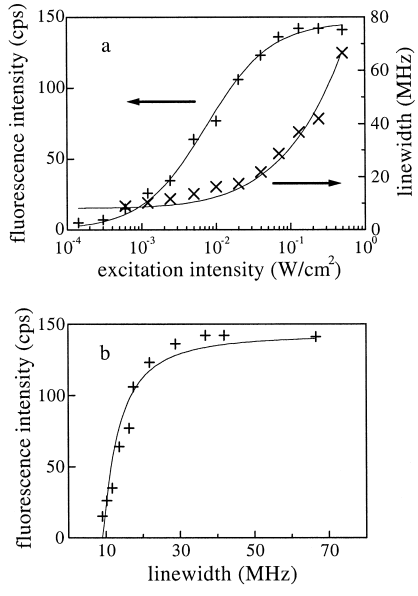

Fig. 3. (a) Saturation curves of the fluorescence signal (left) and the linewidth (right) of a single pentacene molecule (same as in Fig. 2) as a function of the excitation intensity. The solid lines are fits to the common saturation formulae [16]. (b) Fluorescence signal plotted as a function of the linewidth. The solid curve is a fit with the two parameters, homogeneous linewidth (Γ_0) and saturated count rate (R_∞) according to the formula: $R/R_\infty = 1 - (\Gamma_0/\Gamma)^2$.

tion of the polarization of the laser and the transition dipole moment of the molecules. In addition, the saturated count rate depends on the exact axial position of each molecule within the focused excitation beam, which is not well known although the lateral alignment is adjusted such that the fluorescence signal is optimized. In order to circumvent the dependence on the excitation intensity, we plot in Fig. 3b the detected count rate of the fluorescence versus the linewidth as in Ref. [18]. From this plot, we get a more reliable value both for the homogeneous linewidth and the saturating count rate. For the molecule considered above, a homogeneous linewidth of 9.2 MHz and a saturating count rate of 143 cps are derived.

The maximum fluorescence count rate observed for single pentacene molecules in *n*-tetradecane is lower by one order of magnitude than that for pentacene in the O_1 and O_2 sites of *p*-terphenyl [12]. We consider the low count rate to be caused by a much higher value of the ISC yield, which for pentacene is known to vary strongly with the host matrix and in the *p*-terphenyl host crystal even from site to site (0.5% for sites O_1 and O_2, 60% for sites O_3 and O_4 [19]). To obtain a value of the ISC rate for pentacene in *n*-tetradecane, we need to know the triplet lifetime. We have performed time-resolved Optically Detected Magnetic Resonance experiments on an ensemble of pentacene molecules in *n*-tetradecane. In this method, the rates of population and depopulation of the sub-levels of the lowest triplet state are obtained from the transient changes in the fluorescence intensity following microwave pulses which connect the sub-levels [20]. The decay rates of the three sub-levels are found to be

$$k_x = (2.55 \pm 0.1) \times 10^4\ \mathrm{s}^{-1},$$

$$k_y = (3.39 \pm 0.1) \times 10^4\ \mathrm{s}^{-1},$$

$$k_z = (1.58 \pm 0.02) \times 10^3\ \mathrm{s}^{-1}.$$

Together with the normalized steady-state population of the sub-levels

$$n_x = 0.13 \pm 0.03,$$

$$n_y = 0.79 \pm 0.04,$$

$$n_z = 0.08 \pm 0.03,$$

the average triplet lifetime becomes $\tau_T = 33 \pm 3$ μs.

An estimate of the intersystem crossing yield of pentacene in *n*-tetradecane can now be derived. The detection efficiency is given by the product of the quantum efficiency of the photodiode (0.6), the transmission of the dichroic mirror and the red-pass filter (0.2), the transmission of all other optical components (0.5) and the geometrical collection efficiency of the lens (0.035). We observe a maximum detected count rate of 160 cps which means, with a detection efficiency of $0.2 \pm 0.1\%$, that the actual rate of emitted photons $R_\infty^{\mathrm{eff}} = (8 \pm 4) \times 10^4$ photons s^{-1}. The triplet lifetime of 33 μs is much longer than the radiative lifetime of S_1, thus, to good approximation, the molecule undergoes on average $R_\infty^{\mathrm{eff}} \times \tau_T = 2.6 \pm 1$ excitation-emission cycles before entering the triplet state. Consequently, the ISC yield is $40 \pm 20\%$, about equal to the value found for sites O_3 and O_4 of *p*-terphenyl, and almost two orders of magnitude higher than for sites O_1 and O_2.

The value of the ISC rate for pentacene depends strongly on the host matrix and the site. Two models have been proposed to explain such variations. An increase of the ISC rate has been discussed in terms of either a crystal-induced non-planarity of the pentacene molecule [21] or the presence of a higher-lying triplet level T_3 almost in resonance with S_1 [22,23]. Recent studies seem to indicate the prominent role of the latter mechanism. For near-degeneracy, large differences in the ISC rate may result from slight changes in the energy difference between S_1 and T_3 for different matrices or sites. A systematic change of the ISC with the isotopic composition has been observed for pentacene in *p*-terphenyl and interpreted similarly [24].

In order to gain insight into the dynamics of the matrix, we have investigated the spectral behaviour of single pentacene molecules at different optical power levels over several minutes. In these experiments, a succession of spectra is recorded to follow the spectral position of the molecule in time, as displayed in Fig. 4. This way of recording the spectral trajectories of single molecules was applied for the first time for pentacene in *p*-terphenyl [25]. We have selected the molecules at different wavelengths within the inhomogeneously broadened absorption line. In total, we have studied 252 pentacene molecules at various powers, giving us the statistics of 578 traces. These molecules were chosen from

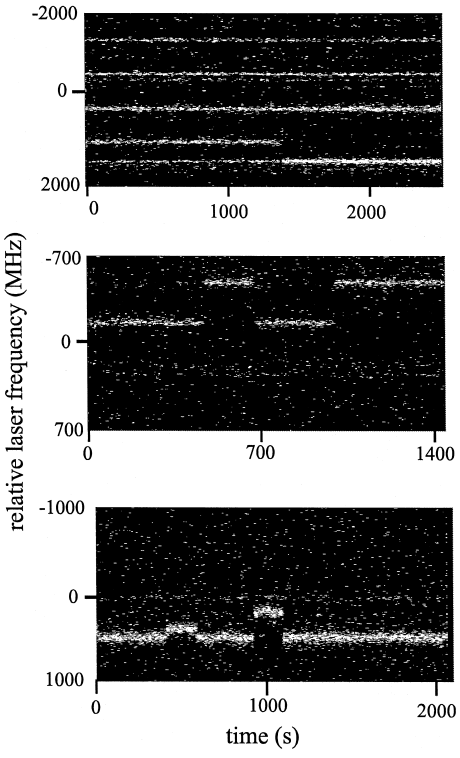

Fig. 4. Three different examples of the spectral trajectories of different pentacene molecules in *n*-tetradecane. Upper panel: Four molecules are stable during all the sweeps (excitation centred at 17094.3 cm^{-1}, 20 mW/cm^2, 2 s/scan). Middle panel: The molecule is coupled to a two-level system (excitation centred at 17090.5 cm^{-1}, 60 mW/cm^2, 3 s/scan). Lower panel: The molecule shows three spectral positions, one of which is occupied more frequently than the other two (excitation centred at 17094.5 cm^{-1}, 40 mW cm^{-2}, 4 s $scan^{-1}$).

different samples which were prepared according to a procedure as reproducible as possible. In all the traces, care is taken to optimize at least the fluorescence signal of one molecule, even though this time-consuming process may have caused the resonances of some molecules to jump outside the spectral detection range before the real start of the measurement.

In order to study the spectral diffusion of single molecules, a good spectral and temporal resolution should be achieved. The low count rate requires a scanning time over the absorption line of one molecule of at least 100 ms, corresponding to a scan rate of 1 MHz ms^{-1}. The frequency stabilization of the laser requires a scan over a range of typically 2 GHz to include at least one absorption line of the iodine cell. Due to these two constraints, a scan time of 2 s results, which is about the delay time between two consecutive observations of the same molecule. Because of the low count rate, 3–4 scans are usually needed to determine the presence of a molecule. As a result, the time resolution of our experiment is about 6 s. Any faster dynamics will not be resolved and will appear as an asymmetry, a broadening, or a splitting of the line of the molecule.

A histogram of the linewidths of the molecules probed with an intensity two times lower than the saturation intensity is displayed in Fig. 5. The profile of the distribution is representative of the dynamics on a timescale faster than our experimental time resolution. We first observe the cut-off width at about 8 MHz close to the homogeneous linewidth of pentacene in *p*-terphenyl. This means that a small number of molecules are not perturbed at all in their environment. The width of the distribution is about 30 MHz and there is no molecule with a linewidth larger than 55 MHz. However, the statistics is rather poor as it is difficult to detect molecules with such a low count rate, especially the ones with a large linewidth.

Consideration of all the molecules reveals that from the 578 traces, only 40 show spectral discontinuities, i.e., jumps in frequency space larger than the linewidth. We have noticed that at an excitation intensity lower than the saturation intensity only 4% of the molecules show spectral diffusion (3 out of 81), while at an excitation intensity higher than the saturation intensity 11.5% of the molecules show instabilities (25 out of 243). This hints that the few

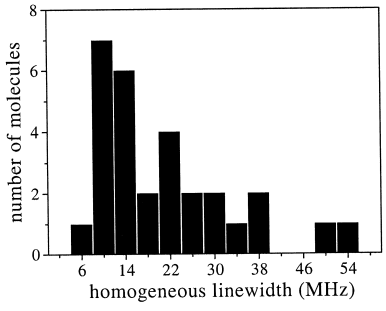

Fig. 5. Histogram of the linewidths of the 29 molecules probed below saturation.

observed spectral jumps may be partly light induced. Even for the molecules that show spectral diffusion, the average number of jumps on the timescale of the experiment (1500 s in average) is only 2.3, which prevents any further analysis of the spectral diffusion behaviour as a function of the excitation intensity.

The good spectral stability of pentacene compared to other molecules investigated in the same type of matrix [7–9] may be related to two factors. The first concerns its dimension. Pentacene fits well into the *n*-tetradecane matrix, thus minimizing the local perturbation around the molecule. Secondly, owing to the high ISC rate, the amount of heat dissipated into the matrix is low even when the molecule reaches saturation. The observed spectral diffusion may be related to a coupling of the pentacene molecules to an ensemble of fluctuating two-level systems. Indeed in several *n*-alkanes, spectral diffusion of terrylene and terrylenediimide molecules was explained by the presence of two-level systems from observations of the distribution and the temperature behaviour of the linewidths [26,27].

4. Summary

In summary, we have observed single pentacene molecules in *n*-hexadecane and *n*-tetradecane. In *n*-tetradecane the low detected photon rate is found to be due to a high ISC yield of about 40%. On a timescale of seconds, little spectral diffusion is observed for pentacene in *n*-tetradecane. Presently we investigate further the perturbations induced by the guest molecule on the host by comparing the spectral diffusion of different molecules in *n*-tetradecane. In particular, we concentrate on the dependence of the spectral properties of single molecules on their spatial position in the polycrystalline Shpol'skii matrix.

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